
III.A.3 SOFC Research and Development in Support of SECA

Objectives

- Explore the effects and mechanisms of chromium migration in SOFCs.

Approach

- Operate cells with E-Brite current collectors and determine voltage degradation rates.
- Identify chromium deposits in cathodes.

Accomplishments

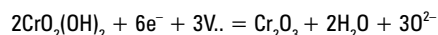
- It was shown that direct contact of a metallic interconnect with the cathode paste/cathode leads to more rapid voltage degradation than expected from the oxyhydroxide mechanism.
- In such cells, a manganese chromium spinel was found near the metal interface, and chromium oxide near the electrolyte.
- It appears that a volatile chromate species, perhaps potassium dichromate, contributes to the degradation.

Future Directions

- The second volatile species will need to be unambiguously identified.
- Methods for diminishing the chromium migration will be explored.

when chromium-containing steels are exposed to oxygen and water at elevated temperatures [1,2]. The volatile oxyhydroxide $\text{CrO}_2(\text{OH})_2$ can form either by reaction of the surface oxide with oxygen and water, or by direct reaction of metallic chromium [3]. It has also been shown that $\text{CrO}_2(\text{OH})_2$ is the dominant species in the gas phase when water is present [4], and that the cathode acts as a nucleation site for the deposition of chromium [5]. Quadackers et al. provide an overview of this and other issues related to metallic-based interconnects [6]. There is also work that indicates that both the cathode and electrolyte composition can play a role in chromium poisoning [7,8].

As discussed by Hilpert and others [9,10], the chromium oxyhydroxide is presumed to be reduced to chromium trioxide at the triple phase boundaries in the cathode as shown:



The oxide deposits block the access of oxygen to the electrochemically active sites and cause the performance decay of the cell. However, the magnitude of the effect varies greatly between cells and stacks from various organizations. To better define the quantitative relations, DOE set up a task force between General Electric, the Pacific Northwest National Laboratory, and Argonne. Our role was to experimentally determine the cell degradation rates in cells with current collectors made of E-Brite, an alloy made by Allegheny Ludlum.

Approach

A new experimental apparatus was jointly developed by the three parties that would simulate the flow field geometry of a typical planar stack. As shown in Figure 1, the fuel cell housing is a two-piece circular structure made of a machinable ceramic (MACOR) that contains a 2.5-cm² metal current collector with five flow channels. Under the channels is a fuel cell consisting of a lanthanum manganite cathode, a zirconia electrolyte and a nickel/zirconia anode. These cells were purchased from InDec.

All the team members used identical fixtures and cells and operated them at 250 mA/cm² and air flow rates of 70 standard cubic centimeters per minute. Argonne ran three types of experiments. In the first, a current collector made of E-Brite was used. In the second the current collector was gold, and in the third, the current collector was E-Brite with the ribs covered with a gold foil. In the first set, chromium oxyhydroxide was expected to form on the channel surfaces and under the ribs. In the second, no oxyhydroxide was expected

Introduction

Chromium contamination of SOFC cathodes has been observed by several groups of researchers developing cells with metallic bipolar plates. Hilpert et al. have attributed the chromium transport to the formation of a volatile oxyhydroxide species that forms

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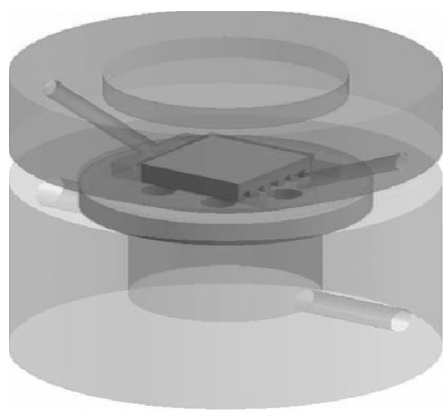


FIGURE 1. Schematic of the Cell Test Stand

to form, and in the third, oxyhydroxide formation was expected only in the channels, where direct contact between E-Brite and cathode is avoided.

Post-test analyses were conducted on the cathodes by scanning electron microscopy and wide-angle X-ray beam spectroscopy using the Advanced Photon Source at Argonne National Laboratory.

Results

Cell Tests

A summary of various electrochemical cell tests is shown in Figure 2. The dark line represents a 1000-hour run with the gold current collector, showing virtually constant performance. In contrast, the cell potential declined rapidly when an E-Brite current collector was used. In that test, a small amount of a yellow deposit was noticed in the exit tube and on the cell after shutdown and disassembly. This yellow deposit was identified as $K_2Cr_2O_7$.

As discussed below, the potassium seems to have come from the MACOR fixture, and to prevent this interference, the MACOR housing was coated with alumina. The lighter trace shows a more stable performance of a cell with an E-Brite current collector in the alumina-coated housing. Finally, a short light trace represents a cell with an E-Brite current collector that had the ribs covered by a gold foil.

Post-test Analyses

Figure 3 shows the distribution of chromium in the cathode. Note that the cathodes consisted of two distinct regions. The layer closest to the electrolyte, labeled as “lower cathode” in the figure contained zirconia to enhance the electrochemical performance, while the “upper cathode” was single-phase strontium-

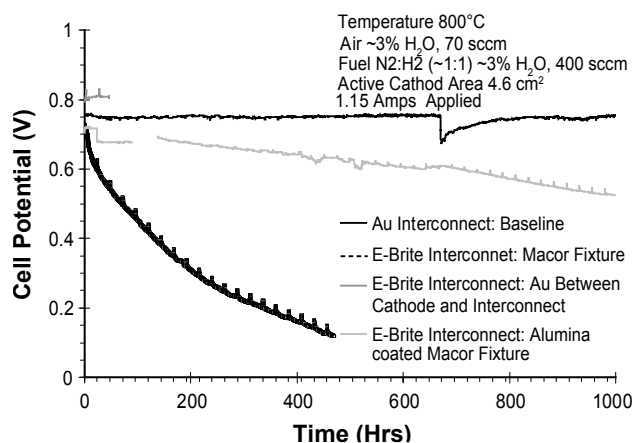


FIGURE 2. Cell Performance Under Various Conditions

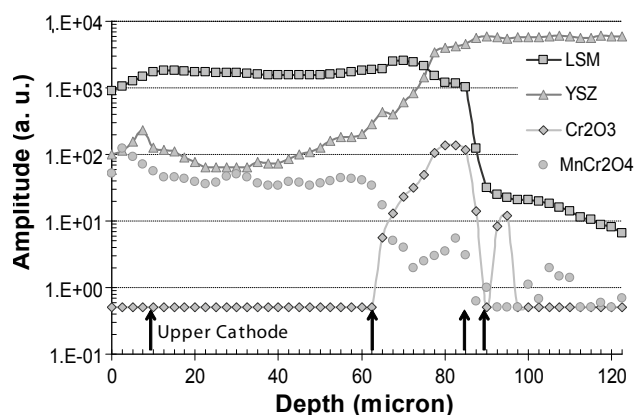


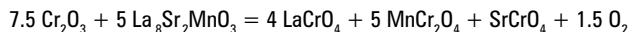
FIGURE 3. Distributions of Cr_2O_3 and $MnCr_2O_4$

doped lanthanum manganite. The figure reveals unambiguously identified Cr_2O_3 deposits (by two distinct X-ray peaks) that are found mostly near the electrolyte but also distributed to some extent in the zirconia-containing part of the cathode. The manganese chromium spinel $MnCr_2O_4$, that has been observed by others, is found primarily near the interconnect interface, and to a lesser extent, throughout the upper cathode. A small rise is noticeable near the electrolyte, as will be discussed further.

Discussion

Our chromium profiles across the cathode clearly show chromium oxide deposits at the electrolyte interface, which is consistent with the mechanism proposed by Hilpert, where the chromium oxyhydroxide is electrochemically reduced to chromium oxide and affects the cell performance. Our profile also confirms that a manganese-chromium spinel forms at the interface of the cathode and the metal. This spinel is the result

of a chemical reaction between the chromium oxide covering the metal and the cathode:



The spinel is confined to the structural part of the cathode and would not seem to affect the electrochemistry. One should note the small amount of spinel near the electrolyte, which, in our view, is formed by the chromium oxide deposits at the electrolyte reacting with the cathode as shown above.

We did not find the spinel phase in cells where the interconnect ribs had been covered with gold foil.

The amount of chromium oxide near the electrolyte was 3-4% in cells that were run in the MACOR fixture and that were rapidly deteriorating. A mass balance calculation that is beyond the scope of this report reveals that the oxyhydroxide mechanism cannot account for the amount of chromium oxide that was detected in the MACOR cells. Since we found potassium dichromate in the exit tube of these cells, we suspect that the latter did contribute to the chromium transport.

We believe it is important to note this finding because potassium oxide is present in many cements, sealants, and glass/ceramic components. If the potassium dichromate can contribute to the chromium migration it could explain the wide range of cell degradation rates reported in the literature.

Conclusions and Future Directions

It appears that the oxyhydroxide mechanism is valid but may have only an insignificant effect on long-term cell performance. Other volatile species such as potassium and/or strontium dichromates seem to contribute to the chromium transport. Future experiments will focus on these compounds.

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Publications/Presentations

1. M. Krumpelt and T. A. Cruse, "Chromium Volatility and Transport in Solid Oxide Fuel Cells," Ceramic Society, Cocoa Beach, FL, January 25-28, 2006.